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# FOREIGN TECHNOLOGY DIVISION

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by

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# EDITED TRANSLATION

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# CALCULATION OF THE THERMODYNAMIC PROPERTIES OF DISSOCIATING NITROGEN TETROXIDE TAKING NONIDEALITY INTO ACCOUNT

V. B. Nesterenko, M. A. Bazhin, and V. P. Bubnov

Recently there has been considerable interest in chemically reactive systems as the most effective working substances [1, 2] for power plants. Nitrogen tetroxide, whose dissociation occurs in the temperature range 290-1500°K,

$$N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$$

290-450-1500

is the most frequently studied of a large class of chemically reactive systems.

In order to perform a thermodynamic analysis of the cycles of power plants on a dissociating working substance and to explain the advantages of such systems, it is necessary to know the enthalpy and entropy in a wide range of temperatures and pressures.

At the present time there is virtually no experimental data on the enthalpy or the heat capacity of the dissociating system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$. It is also impossible to plot thermodynamic diagrams on the basis of experimental P-V-T data since only one work (by W. G. Schlinger and B. H. Sage [3]) has been published on the determination of P-V-T data for $N_2O_4$ in the gaseous phase with a temperature range of 294-440°K and pressures of 1-140 atm (abs).

Based on this, we have attempted to calculate the thermodynamic functions (enthalpy and entropy) using the common thermodynamic relationships and taking into account nonideality for chemically reactive nitrogen tetroxide.

Determining composition. In the thermal dissociation of nitrogen tetroxide

$$N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2 \tag{1}$$

a mixture is formed whose composition changes with a change in pressure and temperature. In order to determine the equilibrium composition of the reactive mixture, the equilibrium constant $K_p$ is used, which, in the case of reaction (1), can be represented in the form

$$K_{p_1} = \frac{4\alpha_1^2(1-\alpha_2)^2}{(1-\alpha_1)(1+\alpha_1+\alpha_1\alpha_2)}P, \tag{2}$$

$$K_{p_2} = \frac{\alpha_1\alpha_2^3}{(1-\alpha_2)^2(1+\alpha_1+\alpha_1\alpha_2)}P. \tag{3}$$

From equations (2) and (3) it follows that in order to determine the molar content of the components in the mixture, it is necessary to know for each value of P and T the size of the equilibrium constants $K_{p_1}$ and $K_{p_2}$.

When we can apply the principle of volume additivity (Amagat's law) to the thermodynamic system, quantities $K_{p_j}$ can be calculated as

$$K_{p_j} = \frac{K_{p_{0j}}}{K_{\gamma_j}}, \tag{4}$$

where quantities $K_{\gamma_j}$ are found from the volatility data of the mixture's components. For the examined reaction (1) quantities $K_{\gamma_j}$ are determined by the relationship

$$K_{\gamma_1} = \frac{\gamma_{N_2O_4}}{\gamma_{NO_2}^2}; \; K_{\gamma_2} = \frac{\gamma_{NO_2}^2}{\gamma_{NO}^2\,\gamma_{O_2}}, \tag{5}$$

in which the coefficient of activity $\gamma_j = \frac{f_j}{P}$.

In view of the fact that the components $N_2O_4$ and $NO_2$ do not exist in pure form, their coefficient of activity was determined on the basis of the experimental P–V–T data of W. G. Schlinger and B. H Sage [3] according to formula

$$\ln \gamma = \int_0^P \left(\frac{V}{RT} - \frac{1}{P}\right) dP. \tag{6}$$

The values of the activity coefficients for components NO and $O_2$ were obtained from the relationship $\gamma = f(\tau, \pi)$ [4].

Based on the obtained data for the activity coefficient, the values of $K_j$ were calculated in the temperature range 300-1500°K and pressure range 1-150 atm (abs).

Since the polynomial of the equilibrium constant obtained by Bodenstein [5] is limited by a temperature range of ~650°K in the first stage of the reaction, we used values for $K_{p_{01}}$ based on a calculation of the isobaric-isothermal potentials for the $N_2O_4$ and $NO_2$ components according to spectroscopic and molecular data [6, 7] and the more precisely defined thermal effect of the hypothetical reaction of a nitrogen tetroxide association, according to the experimental data of Bodenstein and Boüse [8], Verhock and Daniels [9], and Wourtzel [10].

The values for the polynomial of the equilibrium constant $K_{p_{20}}$ were taken from the work of Bodenstein and Lindner [8].

On the basis of the values obtained for $K_{p_{10}}$ and $K_{p_{20}}$ we calculated the equilibrium composition of the chemically reactive system

$$N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2. \tag{7}$$

The thermodynamic functions (enthalpy and entropy) necessary for plotting I–S and T–S diagrams were calculated on the basis of thermodynamic relationships, the thermodynamic theory of empirical

corrections, and generalized tables.

As Hougen, Watson, and Ragatz have shown [11], the molar entropy for real gas can be expressed as

$$S = S_{ideal}p_0 - R \ln (P/P_0) - (S_{ideal} - S)_{p,T}, \tag{8}$$

where the correction for nonideality in terms of relative parameters is calculated thus:

$$(S_{ид} - S)_{P,T} = -R \int_0^{\pi} \frac{(1-z)}{\pi} d\pi + R\tau \int_0^{\pi} \left(\frac{\partial z}{\partial \tau}\right)_{\pi} \frac{d\pi}{\pi}. \tag{9}$$

[ид = ideal]

Hence the value of entropy for the mixture, relative to an initial mole of the nondissociated substance $N_2O_4$, has the form:

$$\begin{aligned} S_{см} = \frac{1}{M_{N_2O_4}} \Bigg\{ & \sum_{j=1}^{m} \left( \frac{n_j}{n_{N_2O_4}} S_{ид j} \right) - \\ & - R \sum_{j=1}^{m} \left[ \frac{n_j}{n_{N_2O_4}} \ln \left( \frac{n_j}{N} \right) - \right. \\ & - \frac{N}{n_{N_2O_4}} R \ln \left( \frac{P}{P_0} \right) - \\ & \left. - \sum_{j=1}^{m} \left[ \frac{n_j}{n_{N_2O_4}} (S_{ид} - S)_j \right] \right\}. \end{aligned} \tag{10}$$

[см = mixture]
[ид = ideal]

In equation (10) the first term represents the entropy of each ideal component in a gaseous phase (8); the next term is the entropy of the mixture; the following term takes into account the variation in entropy from standard pressure to desirable pressure; the last term is the correction for the deviation from ideal gas behavior.

For the examined system the entropy of the mixture is written by analogy with equation (10)

$$S_{см} = \frac{1}{M_{N_2O_4}} \left\{ \left[ (1-\alpha_1) S_{N_2O_4} + 2\alpha_1 (1-\alpha_2) S_{NO_2} + 2\alpha_1\alpha_2 \left( S_{NO} + \right.\right.\right.$$
$$\left.\left. + \frac{1}{2} S_{O_2} \right) \right] - R [(1-\alpha_1) \ln (1-\alpha_1) + 2\alpha_1\alpha_2 \ln 2\alpha_1\alpha_2 + \alpha_1\alpha_2 \ln \alpha_1\alpha_2 +$$
$$+ 2\alpha_1 (1-\alpha_2) \ln 2\alpha_1 (1-\alpha_2) - (1 + \alpha_1 + \alpha_1\alpha_2) \ln (1 + \alpha_1 + \alpha_1\alpha_2)] -$$
$$- [(1-\alpha_1)(S_{нд} - S)_{N_2O_4} + 2\alpha_1 (1-\alpha_2)(S_{нд} - S)_{NO_2} +$$
$$\left.\left. + 2\alpha_1\alpha_2 (S_{нд} - S)_{NO} + \alpha_1\alpha_2 (S_{нд} - S)_{O_2} \right] \right\}. \qquad (11)$$

The enthalpy of the mixture is written as

$$I_{см} = \sum_{j=1}^{m} \frac{n_j I_j}{M_{N_2O_4}}. \qquad (12)$$

In view of the fact that we previously presented a method for calculating the volatility factor, it is advisable to express the correction for nonideality in equations (9) and (12) in terms of the activity coefficient:

$$S_j = S_{0j} - \left[ RT \left( \frac{\partial \ln \gamma_j}{\partial T} \right)_P + R \ln \gamma_j \frac{P}{P_0} \right], \qquad (13)$$

$$I_j = I_{0j} - RT^2 \left( \frac{\partial \ln \gamma_j}{\partial T} \right)_P, \qquad (14)$$

$$\left. \begin{aligned} S_{0j} &= s_{0j} + S_j^0 \\ I_{0j} &= i_{0j} + I_j^0 \end{aligned} \right\}. \qquad (15)$$

The value of quantities $i_{0j}$, $s_{0j}$, $S_j^0$, $I_j^0$ is taken from reference [12].

On the basis of the obtained relationships the values of enthalpy and entropy in the temperature range 300-1500°K and pressure range 1-150 atm (abs) were computed on the Minsk-2 computer at the Computer Center of the BSSR Academy of Sciences.

The values of enthalpy and entropy on the saturation line were obtained from the experimental P-V-T data of Reamer and Sage [13] on the saturation line. The I-S and T-S diagrams which the authors obtained for the dissociating system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ are presented in Figs. 1 and 2.

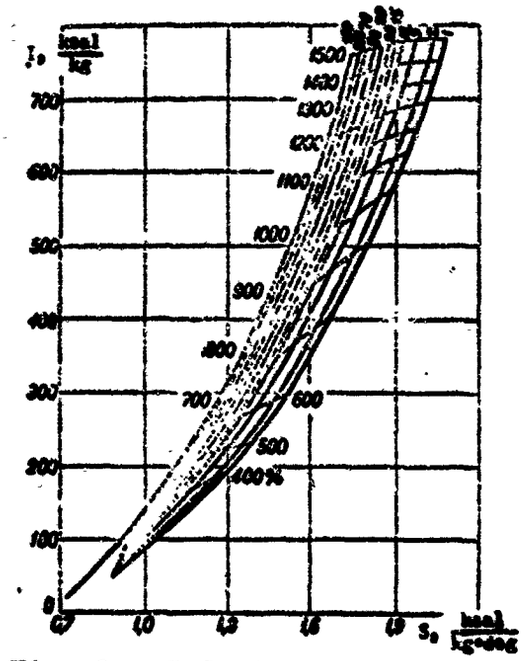


Fig. 1. I–S diagram of the dissociating system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$.

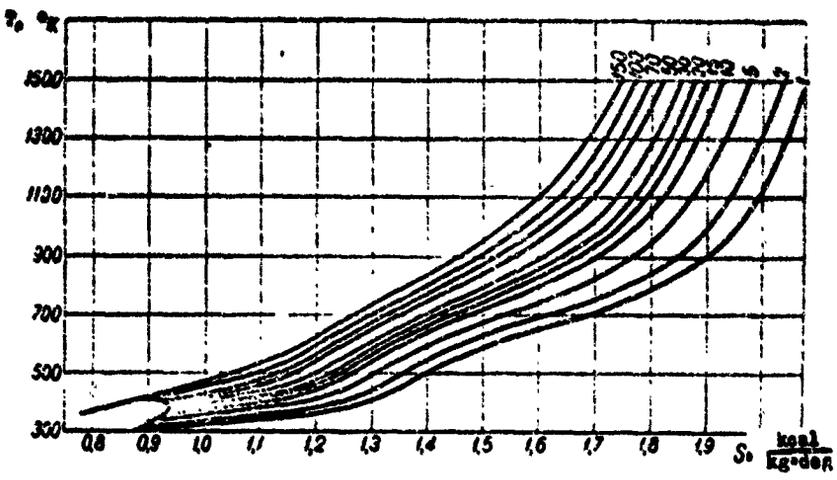


Fig. 2. T–S diagram of the dissociating system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O$.

## Designations

P – total pressure of mixture in $kg/cm^2$; $\alpha_1$, $\alpha_2$ – degree of dissociation of first and second stages in the reaction; $K_{P_{0j}}$ – equilibrium constant as a function of temperature only; $f_j$ – volatility of the j-th component taken at pressure P of mixture; $n_j$ – content of

moles of j-th component in mixture; M – molecular weight; $\pi$ – relative pressure; $\tau$ – relative temperature; T – temperature in °K; z – compressibility factor; $P_0$ – initial pressure; $i_{0j}$, $s_{0j}$ – relative enthalpy and entropy; $I_j^0$, $S_j^0$ – enthalpy and entropy under standard conditions, $N = 1 + \alpha_1 + \alpha_1\alpha_2$.

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ABSTRACT

(U) This study was undertaken because of the lack of experimental data on the enthalpy of dissociating nitrogen tetroxide. At calculation of the entropy (S) and enthalpy (I) of dissociating N(subscript 2)O(subscript 4)was performed in the temperature range 300-1500K and 1-140 atm range, taking into account deviation of the reaching N(subscript 2)O(subscript 4) from ideal behavior. The calculation was carried out on the basis of general thermodynamic functions of the thermodynamic theory of empirical corrections and of generalized tables. The calculated S and I values were used for plotting I-S and T-S diagrams. Orig. art. has: 2 figures.